Peculiarities of structure and phase composition of V-Ti-Cr alloy obtained by sintering technique

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Abstract. Alloy of the V-Ti-Cr system is a promising material exploited under high radiation and in corrosion environment. We sintered V-4.9Ti-4.8Cr alloy from particles with original average size of 30, 280 and 200 μm, respectively for vanadium, titanium and chromium powders, by pressing of the powder mixture and its further sintering. The studies were undertaken using the methods of X-ray structural analysis, scanning electron microscopy with an energy dispersive analyzer and transmission electron microscopy. It was established that the structure of the alloy represented matrix grains (BCC solid solution), along the boundaries and at junctions of which the groups of oxycarbonitride particles of V, Ti, Cr (C,N,O) type of the variable elemental composition were arranged. The particles possessed a plate-like (0.4 × 2.0 μm) and rounded (0.5 μm) shape. The solid solution of the alloy was heterogeneous by concentration. This was evidenced by the complications of the diffraction patterns obtained from the corresponding sections of the structure. These were cords of main reflexes, satellites and emergence of a moire banded contrast in separate sections of the sample. Inside the matrix grains, there were nanoparticles (15 μm) of carbide $V_{55}Cr_{25}C_{20}$, being a source of elastic internal local stresses.

1. Introduction

At present, mineral fuel resources are being built up all over the world. However, use of mineral resources, in particular hydrocarbons, shows that nuclear power engineering does not have alternative fuel competitors. Therefore, development of high-efficiency and radiation-resistant fast neutron reactors is a relevant research topic. The alloy of the V-Ti-Cr system is a promising structural material that will be able to provide optimal performance of parts and components of the reactor under high radiation and corrosive loads [1].

It is known [2] that vanadium-based alloys have the best ‘strength/weight” ratio and high high-temperature characteristics as compared to other construction materials. Possessing less hardness and strength at room and elevated temperatures, these alloys in terms of specific strength surpass stainless

steel and some titanium alloys in the temperature range of 540–650 °C, and in the range of 800–980 °C – the alloys based on nickel, cobalt, molybdenum and niobium.

The alloys of the V-Ti-Cr system have good compatibility with liquid coolants, high strength values at temperatures of 400–700 °C, possess good thermal conductivity and quite high radiation resistance during neutron irradiation. These alloys belong to the category of low-activity alloys, since during neutron irradiation long-lived isotopes that would contribute to the induced activity after several years of exposure are not formed [3].

However, the peculiarity of these alloys is their high chemical activity relatively interstitial impurities (oxygen, carbon, nitrogen) [4]. Therefore, in the process of their production, there is intensive contamination of the material with the mentioned impurities accompanied by formation of oxycarbonitride phases [5-8], being in charge of the high-temperature strength level. In combination with the low solubility of carbon and the high rate of vanadium carbide formation, this leads to the fact that a relatively low concentration of these elements transfers vanadium alloys to a category of heterophase precipitation-hardening alloys with a complex sequence of phase transformations and high sensitivity of dispersity and a nature of distribution of oxycarbonitride phases to insignificant changes of parameters of the work cycle of alloy obtaining. Under these conditions, peculiarities of the heterophase structure exert a significant influence on the regularities and mechanisms of formation of the grain and defective substructure of alloys, its thermal stability, the phase composition of intergranular boundaries, their mobility, and, consequently, the heat resistance level of the alloys, their tendency to low-temperature radiation embrittlement and other structural and sensitive properties, determining the radiation resistance of the material [6,8-12].

In addition, the presence of oxygen, carbon, nitrogen in the material leads to the change in the alloys' chemical composition, which, as a rule, leads to a weakly stable or unstable state of the crystal lattice and, thus, to a structural and phase transformation [13-14].

Therefore, since properties of vanadium alloys depend on the concentration and the state of atoms of oxygen, carbon and nitrogen in them, determined by production technologies and modes of subsequent thermomechanical treatments, when developing these alloys as a material for nuclear power plants of new generation, a necessary stage of the research is the study of their phase composition and the structural state of the alloys immediately after their obtainment. Such analysis is necessary for the purposeful control of the phase and structural state of the alloys when selecting further modes of thermomechanical treatment. To develop the methods of optimizing the thermomechanical treatment of the alloy of the V-Cr-Ti system further, a detailed study of the structural and phase state of the V-4.9Ti-4.8Cr alloy after sintering was carried out in this paper.

2. Material and research techniques

A material of the study was a V-4.9Ti-4.8Cr alloy. To obtain samples of this alloy, powders of the appropriate metals were used. Dispersity of the initial powders was previously studied on a laser device FRITSCH ANALYSETTE 22 intended for measuring particle sizes. The particle sizes were measured according to the principle of laser beam scattering [15].

The average size of original particles of the vanadium powder (VEL-1 brand) was ~ 2 mm; the maximum size of titanium particles (PTS-1 grade) did not exceed 280 μm; that of chromium particles (PHM-1 grade) - 200 μm. Before preparation of the vanadium alloy samples, the initial vanadium powder was subjected to grinding in a planetary mill up to a maximum size of ~ 300 μm.

The process of preparation of the powder mixture, containing 90 mass.% of V – 4.9 mass.% of Ti – 4.8 mass.% of Cr, was carried out as follows. The initial powders were previously dried in the drying cabinet for 1 hour at a temperature of 200 °C. After drying, the vanadium powder was mixed with the powder of titanium and chromium. Then the obtained powder mixture was mixed thoroughly to gain a uniform mass. Stirring of the components was carried out in the closed container for 1 hour.

The process of preparation of the vanadium alloy samples was carried out according to the conventional technology and included pressing of the obtained powder mixture and its further sintering. The homogeneous mass was poured into steel molds with the movable upper die. To mold

the samples, the mold with a diameter of 10 ± 1 mm was used. Pressing of the powders was implemented using the plasticizer in the form of the 3 % aqueous solution of polyvinyl alcohol and was carried out by means of the laboratory press with a maximum load of 15 t (the optimum pressing pressure was selected experimentally up to the maximum value in the absence of stratification of the samples). Sintering was carried out in the high-temperature vacuum furnace Nobertherm with a maximum working temperature of 2200 °C. The sintering regime is shown in Table 1.

Table 1. Temperature regime of sintering of V-4.9Ti-4.8Cr alloy samples.

Initial temperature (T °C)	Final temperature (T °C)	Time (h:min:sec)	Heating rate (°C)/h)
20	350	00:38:40	512
350	1700	02:38:12	512
1700	1750	01:00:00	-
1750	20	00:00:00	-
-	-	Total 4:16:00	-

The studies were carried out using X-ray structural analysis by means of the automatic X-ray diffractometer DRON-3M in $Cu_{k\alpha}$ radiation, scanning electron microscopy using the electron microscope QUANTA 200 3D FEI with the energy-dispersive analyzer INCA SDD X-MAX, and transmission electron microscopy using the electron microscope JEM-2001.

3. Research results

The studies, undertaken using scanning electron microscopy, showed that after sintering, a characteristic peculiarity of the V-4.9Ti-4.8Cr alloy was high heterogeneity of its microstructure throughout the sample cross-section (figure 1a).

As figure 1b shows, the structure of the alloy, obtained with a higher magnification in the electron microscope column, consists of grey (A), light (B) and almost black (C) regions, which is also clearly seen in figure 1a. Figure 1a and figure 1b show clearly that the size and the density of distribution of the regions of different colors (A, B and C) are different. The energy dispersive analysis revealed that the grey regions (A) are V-Ti-Cr matrix grains based on V, the light regions (B) represent also V-Ti-Cr matrix grains based on V, but inside the grains there is a multitude of groups of particles of second phases, the black regions (C) are the regions that are based on Ti. As can be seen from figure 1a, the alloy structure consists of grey and light regions, the size and the distribution density of which are different. The energy dispersive analysis showed that the grey regions are the grains of matrix V-Ti-Cr based on V; the light regions represent regions containing groups of particles of the second phase in addition to the alloy matrix.

The energy dispersive analysis also showed that, although regions A and B represent V-Ti-Cr grains based on V, they differ slightly by the chemical composition. Namely, in the grey regions (A), the Ti content is not higher than 6 wt.%; Cr is not higher than 3 wt.%. In addition to these metals, there are also C, O, N and Si, but their volume fraction is not large (~ 0.2–0.3 wt.% each). In the light regions (B), the Ti content is almost 2 times less (up to 1.5 wt.%), and Cr is almost 4 times more (~ 12 wt.%). Non-metallic elements C, O, N and Si are also present in the light regions, but in significantly large quantities: in various places, the amount of C ranges from 5.0 to 15.0 wt.%, O - from 0.5 to 3 wt.%, N - ~ 1.5 wt % and Si - up to 3 wt.%. Thus, from the analysis it follows that the grey regions are rich in titanium and depleted in chromium; the light regions, on the contrary, are depleted in titanium and rich in chromium. In addition, in the light regions in large quantities, there are such chemical elements as C, O, N and Si, which lead to the formation of particles of second phases. In the black regions, in addition to Ti, the volume fraction of which is more than 60 wt.%, there is V (up to 6 wt.%); Cr is not detected at all, but there are Al and C (2-3 wt.% each) and O, the amount of which in some regions reaches 25 wt.%.

As the studies, conducted using the X-ray structural analysis (XSA method), showed, the alloy matrix is a solid solution having a BCC crystal lattice (space group is Im3m). This agrees with the data of isothermal sections of triple V-Ti-Cr diagrams obtained for different temperatures (from 500 to 1000 ºC) [16].

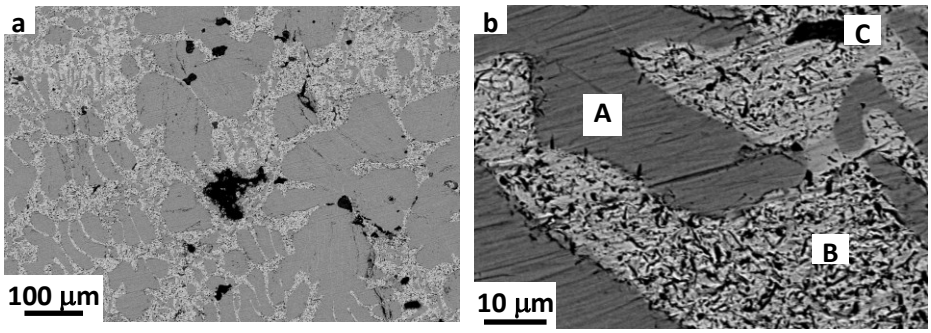

Figure 1. SEM images (a, b) of the V-4.9Ti-4.8Cr alloy after sintering, obtained at different magnifications in the electron microscope column (A – grey regions, B – light regions, C – regions of almost black color).

From the analysis of the triple diagrams it follows that when the Ti concentration in the solid solution changes in the range of 0–20 wt.% and that of Cr - in the range of 0–20 wt.% as well, the crystal lattice must remain cubic body-centered. However, the value of the crystal lattice parameter of the solid solution, depending on the concentration of V, Ti and Cr in it, must vary. This is confirmed by the data presented in figure 2, which shows the concentration dependences of the parameters of crystal lattices of binary solid solutions V-Cr and V-Ti [17].

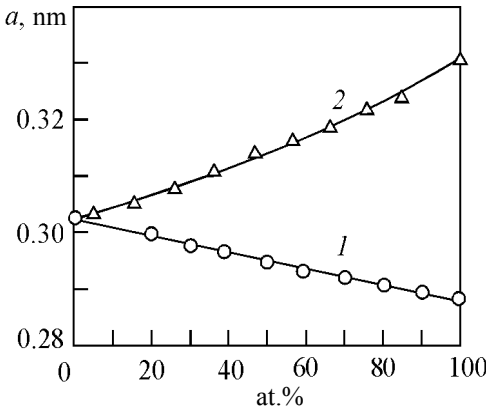

Figure 2. Concentration dependences of crystal lattice parameters of solid solutions V-Cr (curve 1) and V-Ti (curve 2).

The measurements, carried out using the XSA method, showed that the value of the crystal lattice parameter of the V-4.9Ti-4.8Cr alloy under study in different sections of the sample turned out to be different. Its relative change corresponds to a value equal to 0.0003-0.0006 nm. Apparently, this is connected with heterogeneity of distribution of V, Ti and Cr over the sample. This is also confirmed by the energy-dispersive analysis carried out in different sections of the sample. One of such examples is presented in figure 3 (figure 3a shows a SEM-image, figure 3b-d – results of the energy dispersive analysis). Figure 3 shows that vanadium is relatively evenly distributed throughout the sample volume

(figure 3b), but chromium (figure 3c) and titanium (figure 3d) – very unevenly. According to the data of the energy dispersive analysis, the Cr concentration can vary from 1.6 wt.% to 5.7 wt.% even in one grain of the alloy matrix; at the same time, the Ti concentration changes from 0.2 wt.% to 5.9 wt.%.

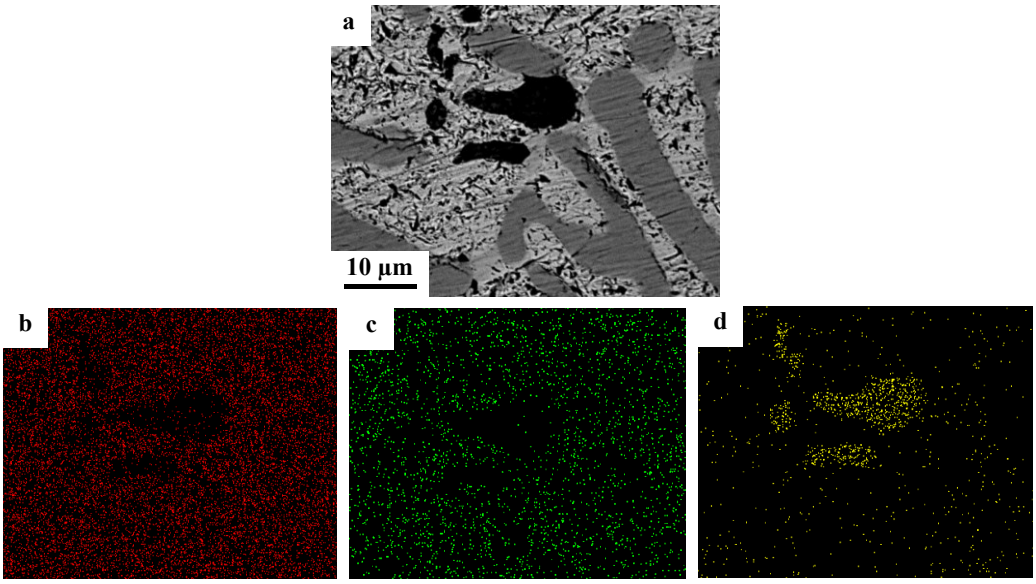

Figure 3. Distribution of V (b), Cr (c) and Ti (d) over the sample section (a). Energy dispersive analysis.

The heterogeneity of the solid solution concentration of the sintered V-4.9Ti-4.8Cr alloy is confirmed by the data of transmission electron microscopy (TEM) presented in figure 4. This figure (figures 4a, 4c and 4e) shows the images of the structure of individual grains of the alloy matrix appropriate for them (figures 4b, 4d and 4f) and their microdiffraction patterns. Heterogeneity by the concentration of the solid solution is justified, first of all, by the complications of the diffraction patterns. First, these are cords of all main reflexes of the alloy matrix (in figure 4b their examples are marked by arrows). Second, this is emergence of satellites also nearby the main reflexes of the alloy matrix (in figure 4d their examples are also marked by arrows). Emergence of cords and satellites is evidence of a microbundle of the solid solution in this section of the material. It should be emphasized that in addition to the microbundle of the solid solution, there is a mesobundle, where the waves of structural irregularity extend over distances of several microns. Therefore, some sections of the sample contain either strands (figures 4a, 4b) or satellites (figures 4c, 4d); others (figures 4e, 4f) – do not. Third, this is emergence of moire banded contrast in separate sections of the sample (figures 4e, 4f), indicating the inconsistency in the two crystal lattices with different parameters or orientations. The obtained data confirmed the fact that in reality the solid solution regions in the phase diagrams were regions where a tendency to stratification existed, since, according to the thermodynamic data, practically all solid solutions were not ideal and would disintegrate under conditions of sufficient diffusion mobility of atoms of the components [18].

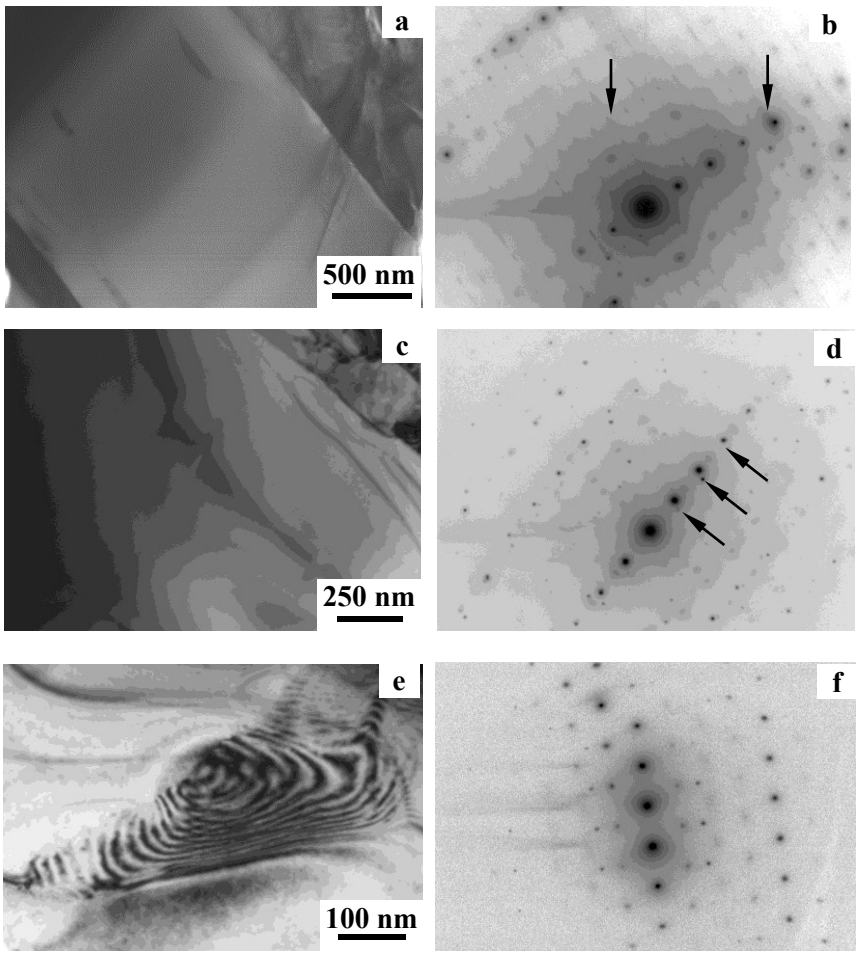

Figure 4. TEM images (a, c, e) and appropriate for them microdiffraction patterns (b, d, f) of individual grains of the V-4.9Ti-4.8Cr alloy after sintering, demonstrating heterogeneity of the solid solution. The arrows in (b) mark examples of cords of main reflexes of the alloy matrix; in (d) – satellites.

The results of thermodynamic modelling of the solid solution regions based on the BCC structure in ternary system Cr-Ti-V using the GALPHAD software were presented earlier in [16]. The calculation results obtained in this paper coincide with the experimental data [19]. In calculations [16], in the framework of the GALPHAD software, experimentally determined thermodynamic data were used, which did not take into account the influence of vacancies and impurities on stability of the solid solution based on the BCC crystal lattice. In the experimentally studied vanadium-based alloys, presented by us and obtained by the sintering method, impurity atoms, which influenced the stability of the solution based on the BCC structure, were present. This was indirectly confirmed in [20] by the influence of vacancies and interstitial defects on mechanical properties in the V–4Cr–4Ti and V-4.9Ti-4.8Cr alloys.

It should be noted that the structures described above (figure 4), evidencing of stratification of the solid solution of the V-4.9Ti-4.8Cr alloy after sintering, can be related to so-called "modulated structures" [21]. That correlates with a theoretically performed calculation of stability of crystal lattices of solid solution V (Ti, Cr) by means of the software package USPEKH using command shell SIESTA [22]. The calculation showed that at a temperature of 0K in solid solution V(Ti,Cr), it is possible to form a stable ordered phase of $V_{18}TiCr$ with an orthorhombic crystal lattice (space group is *Pm*) with the following unit cell parameters: a = 0.5104 nm; b = 0.5111 nm; c = 0.5088 nm. The

presence of a structure with such parameters, determined by the TEM method, is shown experimentally in figures 4a, b.

According to the data of isothermal cross-sections of triple V-Ti-Cr diagrams, the V-4.9Ti-4.8Cr alloy under study is in a single-phase region of the solid solution. There are no other phases in the region of the V-4.9Ti-4.8Cr composition in the state diagrams [16]. However, it is known that one of the main methods of constructing phase diagrams is the results of the XSA method. This method is not local and therefore does not allow detecting highly dispersed phases, especially clusters of atoms of a dissolved component. By means of the XSA method, it is possible to detect a new phase only when the sizes of its particles are greater than the coherent scattering regions of X-rays, and the amount of this phase is not less than 2-5% of the alloy volume. Therefore, if the solid solution has in its structure particles of the new phase, whose dimensions are so small that they are not resolved by the XSA method, then on the phase diagram this alloy is identified only as a solid solution. The studies conducted using the TEM method showed that the solid solution of the alloy under study has particles of a new phase in its structure. Such examples are shown in figures 5-6. In these figures, sections of various grains with precipitated particles of carbide $V_{55}Cr_{25}C_{20}$ are presented (the particles in figure 5a and figure 6a are marked by arrows). This carbide possesses an orthorhombic crystal lattice (space group is *Pmmm*) with parameters a = 0.453 nm, b = 0.5736 nm, c = 0.5012 nm. The microdiffraction patterns obtained from the regions in figures 5a and 6a and presented in figures 5b and 6b, as well as their indicated schemes (figure 5c and figure 6c), confirmed this. The average particle size was 15 nm. It was established that the particles were, as a rule, sources of elastic internal local stresses (figure 5a). Presence of bend dislocation-free extinction contours (in figure 5a, the example of such contour is marked by an arrow of white color and letter "K") pointed to the presence of elastic stresses in the material. The amplitude of these stresses exceeds significantly the yield point value of the alloy under study. Besides, being on dislocations (figure 6), the particles fix them, thereby controlling the processes of primary crystallization of the alloy.

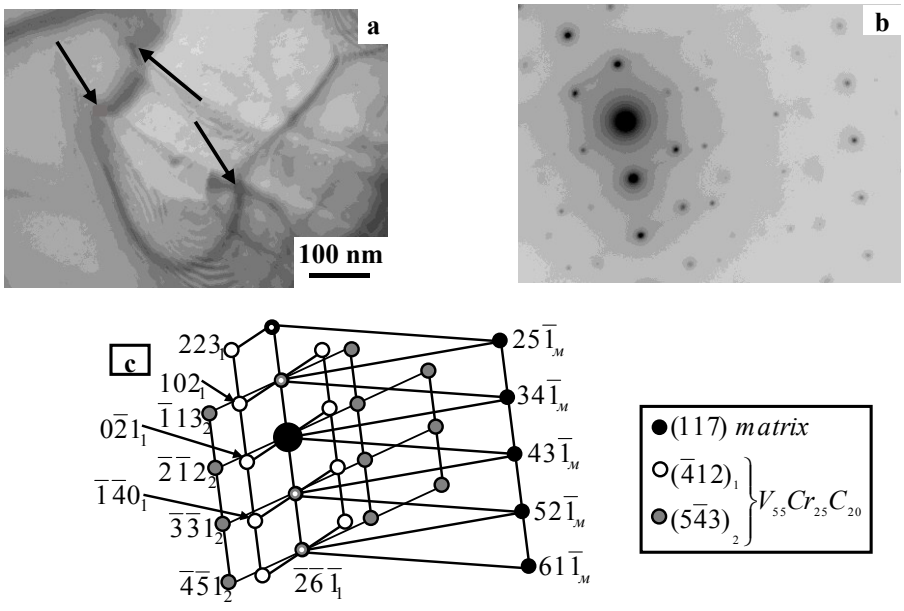

Figure 5. TEM image of the microstructure of the V-4.9Ti-4.8Cr alloy after sintering (a). The arrows point to the particles of carbide $V_{55}Cr_{25}C_{20}$, being sources of internal local stresses (K – bend extinction contour); b - microdiffraction pattern of the section (a); c – its indicated scheme.

It has been noted above that in the alloy there are particles of second phases in the form of separate groups (figure 1). The sizes of the groups and the density of their distribution are different. The particles forming the groups have either a platelet or round shape (figure 1b). The plate-like particles have an average size of 0.4 × 2.0 μm, and the mean diameter of the rounded particles is ~ 0.5 μm.

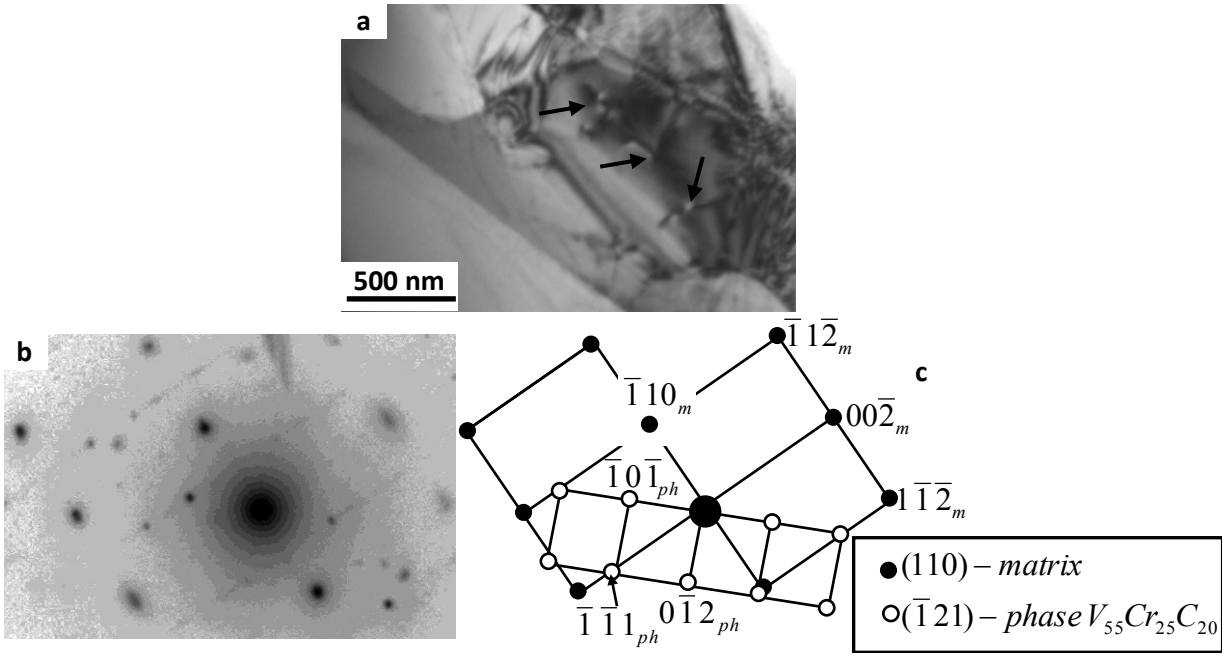

Figure 6. TEM image of the microstructure of the V-4.9Ti-4.8Cr alloy after sintering (a). The arrows point to the particles of carbide V55Cr25C20, fixing dislocations; b - microdiffraction pattern of the section (a); c – its indicated scheme.

Energy dispersion analysis showed that Ti was practically absent from the plate-like particles, but there was a significant amount of V, as well as different amounts of Cr, C and N. Rounded particles contained practically no Cr, but, as well as lamellar precipitates, had a significant amount of V, Ti, O, and C. Analysis of the microdiffraction patterns obtained by the TEM method showed that, regardless of the particles' shape, all precipitates represented an FCC phase, whose lattice parameter varied from 0.413 to 0.430 nm in different particles. Comparison with the existing carbides and nitrides of vanadium, titanium and chromium, possessing FCC crystal lattices, allowed concluding that the particles, formed in the V-4.9Ti-4.8Cr alloy after sintering, were oxycarbonitrides of V, Ti, Cr (C, N, O) type of the variable elemental composition.

Conclusion

The studies undertaken using methods of X-ray structural analysis, scanning electron microscopy with an energy dispersive analyzer and transmission electron microscopy showed that the matrix of the V-4.9Ti-4.8Cr alloy after sintering represented a V(Ti,Cr) solid solution with a BCC crystal lattice. The solid solution was heterogeneous in concentration. This was evidenced by the presence of cords in the main reflexes, satellites and presence of the moire banded contrast in the TEM images. Inside the grains of the V(Ti,Cr) matrix, there were microparticles of orthorhombic carbide $V_{55}Cr_{25}C_{20}$, being sources of internal stress fields. At the junctions and along the grain boundaries, there were aggregates, being in the form of separate groups, of microparticles of the oxycarbonitride of V, Ti, Cr (C, N, O) type of the variable elemental composition with the FCC crystal lattice.

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